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# Synthesis of Novel Polycyclic Selenepinone Compounds

Makoto SAKAKIBARA, Takahiro MIZUMOTO, Yoshihiko WATANABE,
Takeshi TORU, and Yoshio UENO*
Department of Applied Chemistry, Nagoya Institute of Technology,
Gokiso, Showa-ku, Nagoya 466

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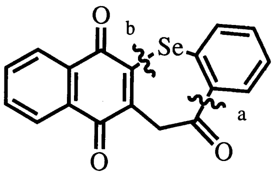
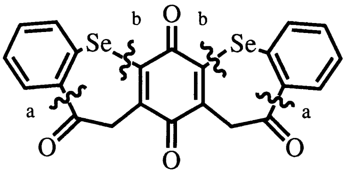
Novel polycyclic selenepinone compounds, benzo[*b*]naphtho[2,3-*f*]selenepin-6,11,13(12*H*)-trione (**6**) and 6, 14-dimethoxybenzo[1,2-*b*:5,4-*b*′]bis[1]benzoselenepin-12,16(13*H*,15*H*)-dione (**14**) were synthesized from chloroquinones.

Previously we reported the synthesis of 4*H*-benzo-[*a*]phenothiazin-4-ones[1] and 4*H*-benzo[*a*]phenoselenazin-4-ones[2] with excellent properties as infrared dyes for semiconductor lasers used for optical recording media.[3] During the course of these studies we found a new method for the generation of benzeneselenolate ion.[4] This provides an efficient preparative method for 2-phenylseleno-1,4-naphthoquinones which can be precursors for the construction of selenium-containing heterocycles. We herein describe the synthesis of novel polycyclic selenepinone compounds, benzo[*b*]naphtho-[2,3-*f*]selenepin-6,11,13(12*H*)-trione (**6**) and 6,14-dimethoxybenzo[1,2-*b*:5,4-*b*′]bis[1]benzoselenepin-12,16(13*H*, 15*H*)-dione (**14**).

Ring closure to the selenepinone is achieved at the *ortho* position of the phenyl by an attack of the carbonyl carbon (bond a in Fig. 1). The phenylseleno group is introduced into quinones by our selenation method (bond b).



Benzo[*b*]naphtho[2,3-*f*]-
selenepintrione



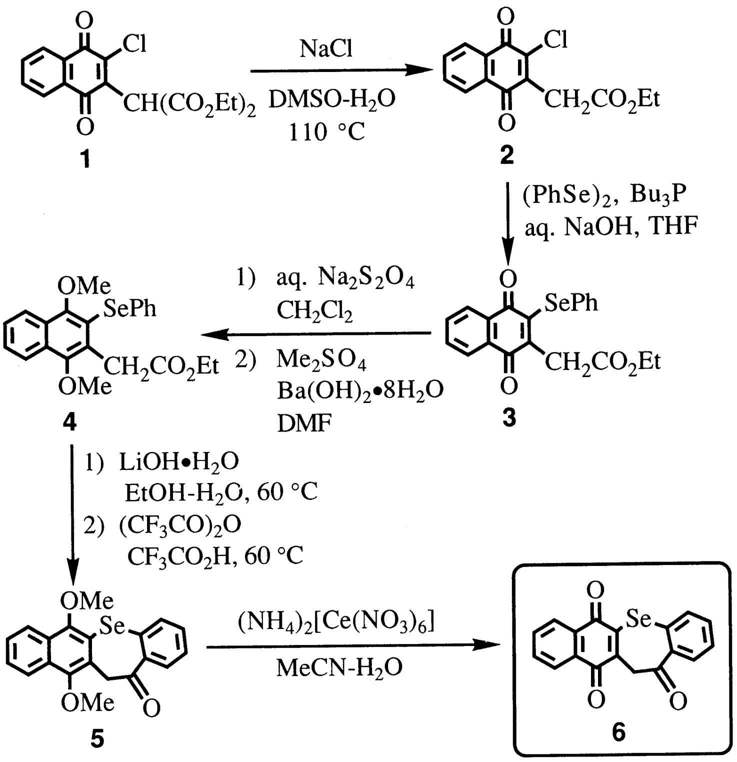
Benzo[1,2-*b*:5,4-*b*′]bis[1]benzoselenepintetraone

Fig. 1.

## Results and Discussion

**Preparation of Benzo[*b*]naphtho[2,3-*f*]selenepin-6,11, 13(12*H*)-trione (6).** Selenation of 2,3-dichloro-1,4-naphthoquinone gave 2-chloro-3-phenylseleno-1,4-naphthoquinone in rather low yield together with a significant amount of 2,3-bis(phenylseleno)-1,4-naphthoquinone. Therefore we planned to prepare ethyl (3-phenylseleno-1,4-naphthoquinon-2-yl)acetate by selenation of ethyl (3-chloro-1,4-naphthoquinon-2-yl)acetate (**2**). Diethyl (3-chloro-1,4-naphthoquinon-2-yl)malonate[5] (**1**) was prepared by the reaction of 2,3-dichloro-1,4-naphthoquinone with sodium malonic ester according to the literature.[6] Decarbonylation of **1** with NaCl in dimethyl sulfoxide (DMSO) and $H_2O$[7] gave (chloronaphthoquinonyl)acetate **2** in 81% yield. Selenation of (chloronaphthoquinonyl)acetate **2** was achieved by our own method[4] as follows: A solution of benzeneselenolate ion was prepared by treatment of a tetrahydrofuran (THF) solution of diphenyl diselenide (0.55 molar amount) and tributylphosphine (0.60 molar amount) with an aqueous NaOH (1.10 molar amount) solution at room temperature for 15 min. Then a solution of benzeneselenolate ion thus obtained was added to a THF solution of **2** and stirred at room temperature for 1 h to give ethyl (3-phenylseleno-1,4-naphthoquinon-2-yl)acetate (**3**) in 95% yield.

First a direct cyclization of the (phenylselenonaphthoquinonyl)acetate **3** to the benzonaphthoselenepintrione **6** was attempted. The acidic conditions due to the use of acid catalysts such as concd $H_2SO_4$, polyphosphoric acid (PPA), or a mixture of $(CF_3CO)_2O$ and $CF_3CO_2H$ resulted in the cleavage of the C–Se bond in **3**, giving diphenyl diselenide together with many unidentified products. In order to remove the acid-fragile nature of **3**, the naphthoquinone framework was converted into the more acid-resistant 1,4-dimethoxynaphthalene. Reduction of the (phenylselenonaphthoquinonyl)acetate **3** with an aqueous $Na_2S_2O_4$ solution gave the [dihydroxy (phenylseleno)naphthyl]acetate, which was then dimethylated with $Me_2SO_4$ in the presence of $Ba(OH)_2\cdot 8H_2O$[8] to afford the [dimethoxy(phenylseleno)naphthyl]acetate **4** in 79% yield. However, exposure of **4** to $(CF_3CO)_2O$ and $CF_3CO_2H$ at 60 °C for 5 h gave only a trace amount of the dimethoxybenzonaphthoselenepinone **5**. All attempts to cyclize **4** to **5** by using various acids were unsuccessful, decomposition of the substrate again predominating. To avoid harsh acidic conditions for the cyclization, we next tried the cyclization of the

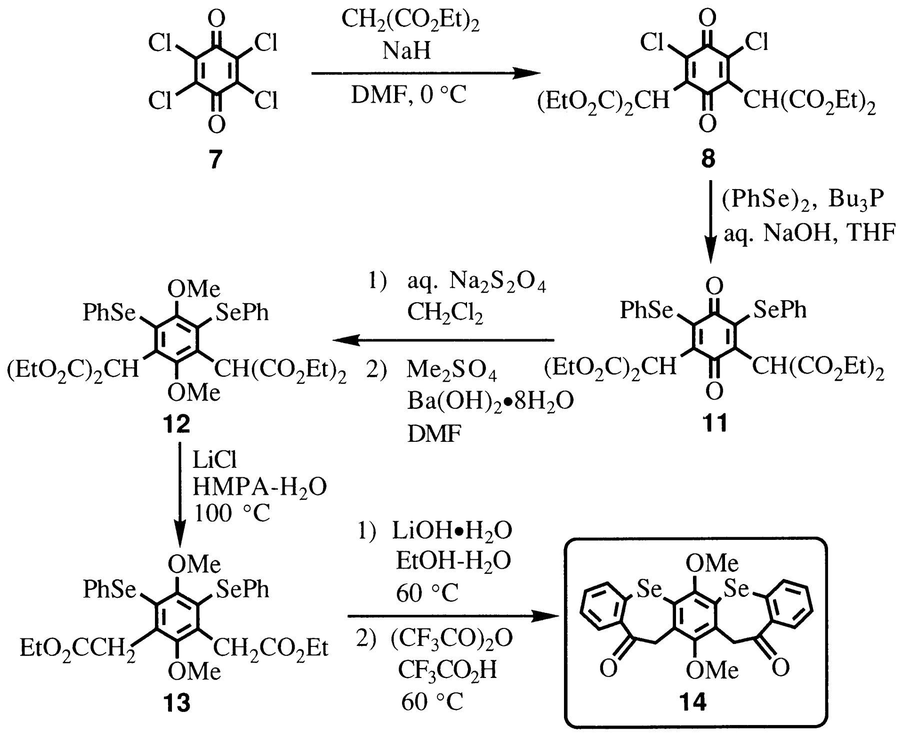


Scheme 1.

carboxylic acid which might be more easily cyclized than the corresponding ester **4**.(9) Thus, hydrolysis of the ester **4** with LiOH in aqueous ethanol gave the carboxylic acid, which was then treated with a mixture of $(CF_3CO)_2O$ and $CF_3CO_2H$ at 60 °C for 5 h to afford dimethoxybenzo[*b*]-naphtho[2,3-*f*]selenepinone **5** in 58% yield. Finally, **5** could be oxidatively demethylated to the benzonaphthoselenepintrione **6** with ammonium hexanitratocerate (IV)(10) in aqueous acetonitrile in 58% yield (Scheme 1).

**Preparation of 6,14-Dimethoxybenzo[1,2-*b*:5,4-*b'*]bis[1]benzoselenepin-12,16(13*H*,15*H*)-dione (14).** We then turned our attention to the construction of a new selenium-containing heterocycle having two selenepinone rings fused to benzoquinone. Treatment of 2,3,5,6-tetrachloro-1,4-benzoquinone (**7**) with 5 equiv of sodium malonic ester in *N,N*-dimethylformamide (DMF)(6) at 0 °C gave two regioisomeric tetraethyl (dichlorobenzoquinonediyl)dimalonates **8** and **9**, and a trisubstituted product, hexaethyl (6-chloro-1,4-benzoquinone-2,3,5-triyl)trimalonate (**10**), in 42, 15, and 14% yield, respectively. In the IR spectrum of **8**, two absorptions due to the carbonyl stretching appeared at 1690 and 1660 $cm^{-1}$, showing the existence of two different carbonyl groups. On the other hand, the IR spectrum of **9** showed a carbonyl stretching at 1675 $cm^{-1}$. Thus, **8** was assigned to tetraethyl (3,5-dichloro-1,4-benzoquinone-2,6-diyl)dimalonate and **9** to tetraethyl (3,6-dichloro-1,4-benzoquinone-2,5-diyl)dimalonate.(11) The (dichlorobenzoquinonediyl)dimalonate **8**, however, was not decarbonylated on treatment with either NaCl in DMSO, NaCN in hexamethylphosphoric triamide (HMPA), or LiCl in HMPA. The (dichlorobenzoquinonediyl)dimalonate **8** was then selenated to tetraethyl [3,5-bis(phenylseleno)-1,4-benzoquinone-2,6-diyl] dimalonate (**11**) (76%) with diphenyl diselenide, tributylphosphine, and an aqueous NaOH solution as described for the preparation of **3**. Reduction of the [bis(phenylseleno)benzoquinonediyl]dimalonate **11** with aqueous $Na_2S_2O_4$ solution into [dihydroxybis-(phenylseleno)phenylene]dimalonate followed by dimethylation with $Me_2SO_4$ in the presence of $Ba(OH)_2 \cdot 8H_2O$ gave tetraethyl [dimethoxybis(phenylseleno) phenylene]dimalonate **12** in 79% yield. Decarbonylation of dimalonate **12** was found to proceed nicely by heating with LiCl in aqueous HMPA at 100 °C for 3 h to give the [dimethoxybis(phenylseleno)phenylene] diacetate **13** in 52% yield. Hydrolysis of the ester **13** followed by cyclization with $(CF_3CO)_2O$ and $CF_3CO_2H$ gave 6,14-dimethoxybenzo[1,2-*b*:5,4-*b'*]bis[1]benzoselenepin-12,16(13*H*, 15*H*)-dione (**14**) in 83% yield (Scheme 2). Unfortunately, demethylation of **14** with ammonium hexanitratocerate (IV) or silver (II) oxide to the quinonoid compound has not been successful.

In summary, the selenation-cyclization reactions starting from chloroquinones provide an efficient route to novel polycyclic selenepinone compounds. Further studies of these heterocycles will be the object of future work.



Scheme 2.

## Experimental

**General.** Melting points were determined with a Yanagimoto micromelting point apparatus and were uncorrected. UV spectra were obtained with a JASCO Ubest-30 spectrometer using 1 cm quartz cells. IR spectra were measured on a JASCO A-102 spectrometer using KBr pellets and/or films. $^1$H NMR spectra were recorded on a JEOL JNM-PMX 60 SI NMR spectrometer in deuteriochloroform, using tetramethylsilane as an internal standard. Mass spectra were obtained with a Hitachi M-2000 spectrometer. Elemental analyses were performed by the Microanalytical Laboratory of Kyoto University. Column chromatography was carried out using Fuji Davison silica gel BW-820MH.

**Ethyl (3-Chloro-1,4-naphthoquinon-2-yl)acetate (2).** A mixture of diethyl (3-chloro-1,4-naphthoquinon-2-yl)malonate[6] (**1**) (4.14 g, 11.8 mmol), NaCl (0.759 g, 13.0 mmol), and water (0.43 ml, 23.9 mmol) in DMSO (3 cm$^3$) was heated at 110 °C for 3 h. Usual workup and purification by column chromatography [hexane–benzene (2 : 8)] yielded **2** (2.66 g, 83%). Yellow plate (from hexane–$CH_2Cl_2$); mp 103.8—105.0 °C; UV ($CHCl_3$) $\lambda_{max}$253 ($\varepsilon$ 18200), 278 (20000), and 341 nm (3400); IR (KBr) 1708, 1670, 1650, 1600, and 1260 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$=1.25 (t, 3H, $J$=7.0 Hz, $CH_3$), 4.90 (s, 2H, $CH_2$), 5.19 (q, 2H, $J$=7.0 Hz, $OCH_2$), 7.57—7.96 (m, 2H), and 7.96—8.37 (m, 2H). Found: C, 60.44; H, 4.17%. Calcd for $C_{14}H_{11}ClO_4$: C, 60.33; H, 3.99%.

**Ethyl (3-Phenylseleno-1,4-naphthoquinon-2-yl)acetate (3).** A THF (0.5 cm$^3$) solution of diphenyl diselenide (152 mg, 0.486 mmol) and tributylphosphine (0.132 cm$^3$, 0.530 mmol) was vigorously stirred at room temperature under argon for 5 min. Then a 10% aqueous NaOH solution (0.35 cm$^3$, 0.972 mmol) was added, and the mixture was stirred for 15 min, during which time the two-phase mixture became homogeneous and the yellow solution turned colorless. The resulting mixture was then added dropwise to a THF (0.5 cm$^3$) solution of (chloronaphthoquinonyl)acetate **2** (247 mg, 0.884 mmol) at room temperature under argon and the solution was stirred for an additional 1 h. Usual workup and purification by column chromatography [hexane–EtOAc (95 : 5)] gave **3** (336 mg, 95%). Orange needle (from hexane–$CH_2Cl_2$); mp 79.1—80.2 °C; UV ($CHCl_3$) $\lambda_{max}$ 256 ($\varepsilon$ 30200), 337 (5200), and 446 nm (2800); IR (KBr) 1737, 1655, 1588, 1572, and 1271 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$=1.22 (t, 3H, $J$=7.0 Hz, $CH_3$), 3.92 (s, 2H, $CH_2$), 4.10 (q, 2H, $J$=7.0 Hz, $OCH_2$), 6.93—7.42 (m, 3H), 7.42—7.82 (m, 4H), and 7.82—8.22 (m, 2H); MS $m/z$ (rel intensity, %) 400 (M$^+$, 60), 398 (M$^+$, 31), 355 (12), 326 (18), 243 (65), 215 (100), 187 (75), 157 (22), 142 (11), and 114 (55). Found: C, 59.87; H, 3.99%. Calcd for $C_{20}H_{16}O_4Se$: C, 60.15; H, 4.05%.

**Ethyl (1,4-Dimethoxy-3-phenylseleno-2-naphthyl)acetate (4).** In a separatory funnel were placed a red solution of (phenylselenonaphthoquinonyl)acetate **3** (0.262 g, 0.657 mmol) in dichloromethane (10 cm$^3$) and an aqueous solution (20 cm$^3$) of $Na_2S_2O_4$ (85% purity, 2.016 g, 9.85 mmol). Then the separatory funnel was shaken until the organic layer became colorless. The aqueous layer was extracted with dichloromethane and evaporated to give the crude hydroquinone. To this crude hydroquinone was added $Ba(OH)_2 \cdot 8H_2O$ (0.228 g, 0.723 mmol) and DMF (2 cm$^3$), and the resulting mixture was stirred at room temperature under argon for 5 min. Then, $Me_2SO_4$ (0.190 cm$^3$, 2.01 mmol) was added and the solution was stirred overnight. Usual workup and purification by column chromatography [hexane–EtOAc (9 : 1)] gave **4** (0.223 g, 79%). UV ($CHCl_3$) $\lambda_{max}$ 333 nm ($\varepsilon$ 2600); IR (film) 1727, 1572, and 1348 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$=1.20 (t, 3H, $J$=7.0 Hz, $CH_3$), 3.90 (s, 3H, $OCH_3$), 3.94 (s, 3H, $OCH_3$), 4.10 (q, 2H, $J$=7.0 Hz, $OCH_2$), 4.13 (s, 2H, $CH_2$), 7.02—7.30 (m, 5H), 7.42—7.70 (m, 2H), and 7.98—8.28 (m, 2H); MS $m/z$ (rel intensity, %) 430 ($M^+$, 100), 428 ($M^+$, 53), 415 (10), 385 (5.0), 355 (9.5), 327 (16), 273 (28), 213 (34), and 173 (18). Found: C, 61.45; H, 5.17%. Calcd for $C_{22}H_{22}O_4Se$: C, 61.54; H, 5.16%.

**6,11-Dimethoxybenzo[*b*]naphtho[2,3-*f*]selenepin-13(12*H*)-one (5).** To an ethanol (2 $cm^3$) solution of (dimethoxyphenylselenonaphthyl)acetate **4** (65 mg, 0.15 mmol) was added an aqueous solution (2 $cm^3$) of $LiOH{\cdot}H_2O$ (32 mg, 0.75 mmol) and the mixture was heated at 60 °C for 4.5 h. The ice-cooled mixture was acidified with 1 M HCl (1 M=1 mol $dm^{-3}$), extracted with ether, and evaporated to give the crude carboxylic acid. This crude carboxylic acid was dissolved in a mixture of $(CF_3CO)_2O$ (0.58 $cm^3$) and $CF_3CO_2H$ (1.16 $cm^3$) and the resulting solution was heated at 60 °C for 5 h. Usual workup and purification by column chromatography [hexane–EtOAc (98 : 2)] gave **5** (31 mg, 54%). White crystal (from hexane–$CH_2Cl_2$); mp 167.3—168.5 °C; UV ($CHCl_3$) $\lambda_{max}$ 280 ($\varepsilon$ 5200) and 324 nm (2400); IR (KBr) 1663, 1567, and 1352 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$=3.96 (s, 3H, $OCH_3$), 4.02 (s, 3H, $OCH_3$), 4.63 (s, 2H, $CH_2$), 7.27—7.72 (m, 4H), and 7.72—8.34 (m, 4H); MS $m/z$ (rel intensity, %) 384 ($M^+$, 100), 382 ($M^+$, 56), 369 (10), 353 (56), 304 (88), 289 (96), 271 (24), and 104 (35). Found: C, 62.74; H, 4.07%. Calcd for $C_{20}H_{16}O_3Se$: C, 62.67; H, 4.21%.

**Benzo[*b*]naphtho[2,3-*f*]selenepin-6,11,13(12*H*)-trione (6).** To an acetonitrile (2 $cm^3$) solution of dimethoxybenzo[*b*]naphtho[2,3-*f*]selenepinone **5** (30 mg, 0.078 mmol) was added dropwise a solution of ammonium hexanitratocerate (IV) (258 mg, 0.470 mmol) in water (1 $cm^3$). The mixture was stirred at room temperature for 3 h. Usual workup and purification by column chromatography (benzene) gave **6** (16 mg, 58%). Red plate (from hexane–$CH_2Cl_2$); mp 209.0—211.0 °C; UV ($CHCl_3$) $\lambda_{max}$ 251 ($\varepsilon$ 31600), 304 (8100), 329 (8100), and 455 nm (2800); IR (KBr) 1658, 1582, 1570, 1560, 1279, and 1267 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$=4.30 (s, 2H, $CH_2$), 7.25—7.58 (m, 2H), 7.58—7.93 (m, 3H), and 7.93—8.35 (m, 3H); MS $m/z$ (rel intensity, %) 354 ($M^+$, 62), 352 ($M^+$, 34), 274 (100), 246 (57), 218 (33), and 104 (59). Found: C, 61.28; H, 2.99%. Calcd for $C_{18}H_{10}O_3Se$: C, 61.21; H, 2.85%.

**Tetraethyl (3,5-Dichloro-1,4-benzoquinone-2,6-diyl)dimalonate (8).** To a suspension of sodium hydride (60% dispersion in mineral oil, 9.76 g, 407 mmol) in DMF (50 $cm^3$) was added dropwise diethyl malonate (61.7 $cm^3$, 407 mmol) under a nitrogen stream at 0 °C. After being stirred for 4.5 h, the mixture was added to a suspension of tetrachlorobenzoquinone **7** (20.0 g, 81.3 mmol) in DMF (30 $cm^3$), and then stirred for an additional 1 h. Usual workup and purification by column chromatography [hexane–EtOAc (85 : 15)] gave **8** (16.8 g, 42%) together with **9**[11] (6.07 g, 15%) and **10** (7.02 g, 14%).

**8:** UV ($CHCl_3$) $\lambda_{max}$ 281 nm ($\varepsilon$ 12600); IR (film) 1720, 1690, 1660, 1370, 1307, 1240, 1180, 1157, and 1040 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$=1.33 (t, 12H, $J$=7.0 Hz, 4×$CH_3$), 4.26 (q, 8H, $J$=7.0 Hz, 4×$OCH_2$), and 5.00 (s, 2H, 2×CH). Found: C, 48.48; H, 4.38%. Calcd for $C_{20}H_{22}Cl_2O_{10}$: C, 48.69; H, 4.50%.

**9:** Yellow needle (from hexane–$CH_2Cl_2$); mp 136.0—137.0 °C (lit,[11] mp 132 °C); UV ($CHCl_3$) $\lambda_{max}$ 279 nm ($\varepsilon$ 12000); IR (KBr) 1720, 1675, 1320, 1290, 1222, 1190, and 1027 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$=1.31 (t, 12H, $J$=7.0 Hz, 4×$CH_3$), 4.28 (q, 8H, $J$=7.0 Hz, 4×$OCH_2$), and 5.01 (s, 2H, 2×CH). Found: C, 48.57; H, 4.54%. Calcd for $C_{20}H_{22}Cl_2O_{10}$: C, 48.69; H, 4.50%.

**10:** UV ($CHCl_3$) $\lambda_{max}$ 276 nm ($\varepsilon$ 11000); IR (film) 2960, 1725, 1665, 1360, 1310, 1240, 1170, 1150, 1012, and 726 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$=1.27 (t, 18H, $J$=7.0 Hz, 6×$CH_3$), 4.24 (q, 12H, $J$=7.0 Hz, 6×$OCH_2$), and 5.05 (s, 3H, 3×CH). Found: C, 52.52; H, 5.41%. Calcd for $C_{27}H_{33}ClO_{14}$: C, 52.55; H, 5.40%.

**Tetraethyl [3,5-Bis(phenylseleno)-1,4-benzoquinone-2,6-diyl]dimalonate (11).** A mixture containing benzeneselenolate ion, which was generated from diphenyl diselenide (128 mg, 0.411 mmol), tributylphosphine (0.115 $cm^3$, 0.46 mmol), and a 10% aqueous NaOH solution (0.30 $cm^3$, 0.83 mmol) as described for the preparation of **3**, was added to a THF (0.4 $cm^3$) solution of (dichlorobenzoquinonediyl)dimalonate **8** (185 mg, 0.374 mmol) under an argon atmosphere. The mixture was then stirred at room temperature for 1 h. Usual workup and purification by column chromatography [hexane–EtOAc (8 : 2)] gave **11**(209 mg, 76%). UV ($CHCl_3$) $\lambda_{max}$ 266 ($\varepsilon$ 33900) and 452 nm (1900); IR (film) 1740, 1703, 1680, 1580, 1320, 1306, 1255, 1247, 1210, 1180, 1155, and 1030 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$=1.02 (t, 6H, $J$=7.0 Hz, 2×$CH_3$), 1.25 (t, 6H, $J$=7.0 Hz, 2×$OCH_2$), 4.07 (q, 4H, $J$=7.0 Hz, 2×$OCH_2$), 4.14 (q, 4H, $J$=7.0 Hz, 2×$CH_3$), 5.10 (s, 2H, 2×CH), and 6.78—7.54 (m, 10H). Found: C, 52.07; H, 4.26%. Calcd for $C_{32}H_{32}O_{10}Se_2$: C, 52.32; H, 4.40%.

**Tetraethyl [2,5-Dimethoxy-4,6-bis(phenylseleno)-1,3-phenylene]dimalonate (12).** Reduction of [bis(phenylseleno)benzoquinonediyl]dimalonate **11** (0.862 g, 1.17 mmol) with $Na_2S_2O_4$ (85% purity, 3.60 g, 17.6 mmol) and subsequent dimethylation with $Ba(OH)_2{\cdot}8H_2O$ (0.407 g, 1.29 mmol) and $Me_2SO_4$ (0.33 $cm^3$, 3.48 mmol) in DMF (1 $cm^3$) (10 h), as described for the preparation of **4**, gave **12** (0.713 g, 79%). White needle (from hexane–$CH_2Cl_2$); mp 111.5—112.0 °C; UV ($CHCl_3$) $\lambda_{max}$ 255 ($\varepsilon$ 15500) and 311 nm (7100); IR (KBr) 1720, 1575, 1380, 1312, 1300, 1262, 1240, 1162, 1027, and 1010 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$=1.23 (t, 12H, $J$=7.0 Hz, 4×$CH_3$), 3.77 (s, 6H, 2×$OCH_3$), 4.07 (q, 4H, $J$=7.0 Hz, 2×$OCH_2$), 4.13 (q, 4H, $J$=7.0 Hz, 2×$OCH_2$), 5.47 (s, 2H, 2×CH), and 6.90—7.25 (m, 10H). Found: C, 53.52; H, 4.94%. Calcd for $C_{34}H_{38}O_{10}Se_2$: C, 53.40; H, 5.02%.

**Diethyl [2,5-Dimethoxy-4,6-bis(phenylseleno)-1,3-phenylene]diacetate (13).** A mixture of [dimethoxybis(phenylseleno)phenylene]dimalonate **12** (1.739 g, 2.27 mmol) and LiCl (0.482 g, 11.37 mmol) in a mixture of HMPA (10 $cm^3$) and water (0.33 $cm^3$, 18.3 mmol) was heated at 100 °C for 3 h. Usual workup and purification by column chromatography [hexane–EtOAc (9 : 1)] gave **13** (0.731 g, 52%). UV ($CHCl_3$) $\lambda_{max}$ 255 ($\varepsilon$ 14500) and 306 nm (5400); IR (film) 1725, 1575, 1438, 1380, 1365, 1321, 1220, 1170, 1030, and 1018 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$=1.20 (t, 6H, $J$=7.0 Hz, 2×$CH_3$), 3.67 (s, 3H, $OCH_3$), 3.75 (s, 3H, $OCH_3$), 4.02 (s, 4H, 2×$CH_2$), 4.07 (q, 4H, $J$=7.0 Hz, 2×$OCH_2$), and 6.93—7.40 (m, 10H); MS $m/z$ (rel intensity, %) 622 ($M^+$, 100), 620 ($M^+$, 93), 618 ($M^+$, 56), and 465 (32). Found: C, 53.98; H, 4.87%. Calcd for $C_{28}H_{30}O_6Se_2$: C, 54.20; H, 4.88%.

**6,14-Dimethoxybenzo[1,2-*b*:5,4-*b′*]bis[1]benzoselenepin-12,16(13*H*, 15*H*)-dione (14).** In a manner similar to the preparation of **5**, hydrolysis of [dimethoxybis(phenylseleno)-phenylene]diacetate **13** (0.62 g, 1.0 mmol) with $LiOH{\cdot}H_2O$ (420 mg, 10.0 mmol) and subsequent treatment with $(CF_3CO)_2O$ (4.2 $cm^3$) and $CF_3CO_2H$ (2.1 $cm^3$) (at 60 °C for 12 h) afforded **14** (0.438 g, 83%). White needle (from hexane–$CH_2Cl_2$); mp 257.5—259.0 °C; UV ($CHCl_3$) $\lambda_{max}$ 309 ($\varepsilon$ 16200) and 341 nm (8700); IR (KBr) 1668, 1580, 1387, 1280, and 1209 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$=3.85 (s, 3H, OCH$_3$), 3.98 (s, 3H, OCH$_3$), 4.47 (s, 4H, 2×CH$_2$), 7.01—7.59 (m, 4H), 7.59—7.95 (m, 2H), and 8.07—8.51 (m, 2H); MS $m/z$ (rel intensity, %) 530 (M$^+$, 100), 528 (M$^+$, 91), 526 (M$^+$, 55), 499 (43), 497 (40), and 495 (23). Found: C, 54.61; H, 3.14%. Calcd for $C_{24}H_{18}O_4Se_2$: C, 54.56; H, 3.43%.

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